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Enclosure 1

Solubility of Lead Phthalocyanine in Various Polymers and their NLO Properties

Solubility of lead phthalocyanine was investigated in polycarbonate (PC), polymethyl methacrylate (PMMA), styrene acrylonitrile (SAN25) and polyethylene terephthalate (PET) as seen in figure 2. Lead phthalocyanine dye exhibited maximum solubility in polycarbonate indicated by the high monomer/dimer ratio. Solubility of lead phthalocyanine was also investigated in two polyesters- polyethylene terephthalate (PET) and polyethylene naphthanate (PEN). The dissolution of $\text{PbPc}(\text{CP})_4$ in these polyesters resulted in the formation of a metal-free phthalocyanine. These compounds have been known to exhibit a characteristic four peak pattern in the UV-VIS spectrum as seen in figure 3. Formation of these metal free phthalocyanines is not desirable as they have inferior NLO properties compared to phthalocyanines with metal. Since polycarbonate was the best host candidate amongst the materials studied, the effect of lead phthalocyanine concentration in polycarbonate was investigated in greater detail. Figure 4 indicates that lead phthalocyanine is soluble in polycarbonate up to 10% by weight. This is shown by a large monomer/dimer ratio in the UV- absorption spectrum. The picosecond-nanosecond response of these polycarbonate-lead phthalocyanine blends was studied using degenerate four wave mixing (DFWM) experiments. Figure 5 shows that the excited state is formed within 10 picoseconds and has a lifetime longer than 20 nanoseconds regardless of the composition. Incorporation of the dye increased the density and hence the refractive index of Polycarbonate (See Appendix). The NLO properties of the PC-lead dye melt blends were compared with those of lead dye-chloroform solution. Figure 6 shows that the melt blends have lower optical limiting thresholds and better efficiency.

Fabrication, Characterization and NLO Properties of 1D Photonic Crystal Limiters

The first non-linear nanolayer materials were fabricated with PET layers alternating with PC- lead phthalocyanine blend (7.5% by weight) layers. A 512 layer composite consisting of 150 nm thick individual layers was designed. The layer structure was confirmed with atomic force microscopy. AFM images in figure 7 indicate average layer thickness of ~ 160 nm. Areas with relatively uniform thickness were selected from these films for the NLO measurements. Presence of interference fringes in reflection spectrum indicated relatively uniform thickness (figures 8 and 9). These areas were rather small (smaller than 5 mm^2) and the film as a whole had a "streaky" appearance as can be seen in figure 13. Even a very small, apparently uniform area of the streaked film has low transmission and a very broad reflection spectrum as seen in figure 14. (for more details on the issue of obtaining large areas of uniform thickness and our recent breakthrough regarding that, please refer to the next section- "Process Breakthrough in making 1D Photonic Crystals") .Non-linear transmission measurements were carried out on these selected areas. Figure 10 shows the non-linear transmission response of this nanolayer film. The figure shows that the limiting thresholds are lower and the limiting coefficients higher for the layered materials compared to a typical non-linear absorber. This observation has led us to the conclusion that, non-linear reflectivity is "active" in the layered materials in addition to non-linear absorption. As the laser wavelength approached the photonic band gap of the layered composite (750 nm), the response of the layered material started deviating from the monolithic material significantly (Figure 11). This reinforces the additional synergistic contribution of non-linear reflectivity in these nanolayered systems.

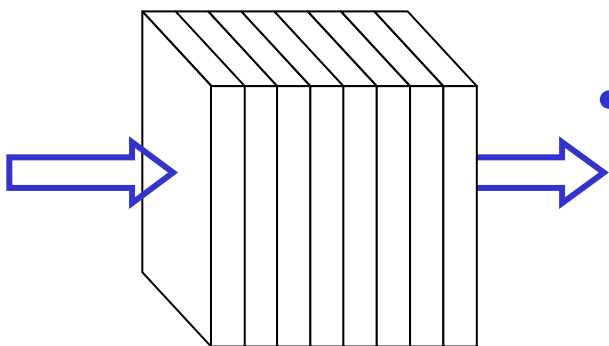
Process Breakthrough in making 1D Photonic Crystals

Until recently, it was not possible to achieve the high level of layer uniformity over the entire assembly that the non-linear optical limiting applications require. A breakthrough in process development has largely removed this obstacle and vastly expanded the opportunities for layer-multiplying technology. It is now possible to produce nanolayer films with large areas in which pre-determined narrow reflection bands can be realized.

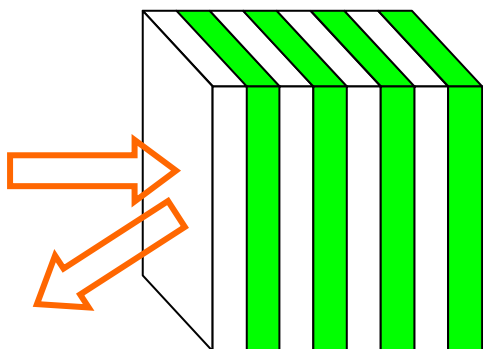
The breakthrough was enabled by insertion of skin layers of a third polymer at the end of the layer-multiplication process as seen in Figure 12. The skin layers serve at least two functions: (1) to remove surface instabilities that cause roughness and streaking as the film exits the die, and (2) to enable fabrication of very thin assemblies with fewer layers. Multiaxial stretching with the recently installed Brückner Karo IV machine further improves film properties. If properly chosen, the skin layer can be peeled off as the last step in the fabrication process.

The magnitude of the breakthrough that will enable realization of these opportunities is visually illustrated in Figure 13 where the streaked, multi-colored appearance of a film processed without skin layers is contrasted with a large area of homogeneous color in a biaxially stretched film after the skin layers were removed. Low transmission and a very broad reflection band characterize the transmission spectrum from even a very small, apparently uniform area of the streaked film as seen in figure 14. In contrast, the new film exhibits high transmission and a very narrow reflection band. Comparison with model simulations suggests highly uniform layers with a standard deviation in thickness of about 12%. The control of layer thickness achievable in this system is shown in figure 15. Pre-designed purple, green and red films are produced by controlling the individual layer thickness in the composite. Exploitation of this flexible process

technology will lead the development of a new generation of nonlinear 1D photonic band gap devices based on organic materials.



- **Low Intensity**
 - Refractive indices are matched and film is transparent



- **High Intensity**
 - Index of one component changes
 - Index matching lost
- **Photonic Band Gaps Develop**
 - Light is reflected

Figure 1
Approach to combining non-linear absorption and non-linear reflection to achieve non-linear optical properties via nanolayered systems

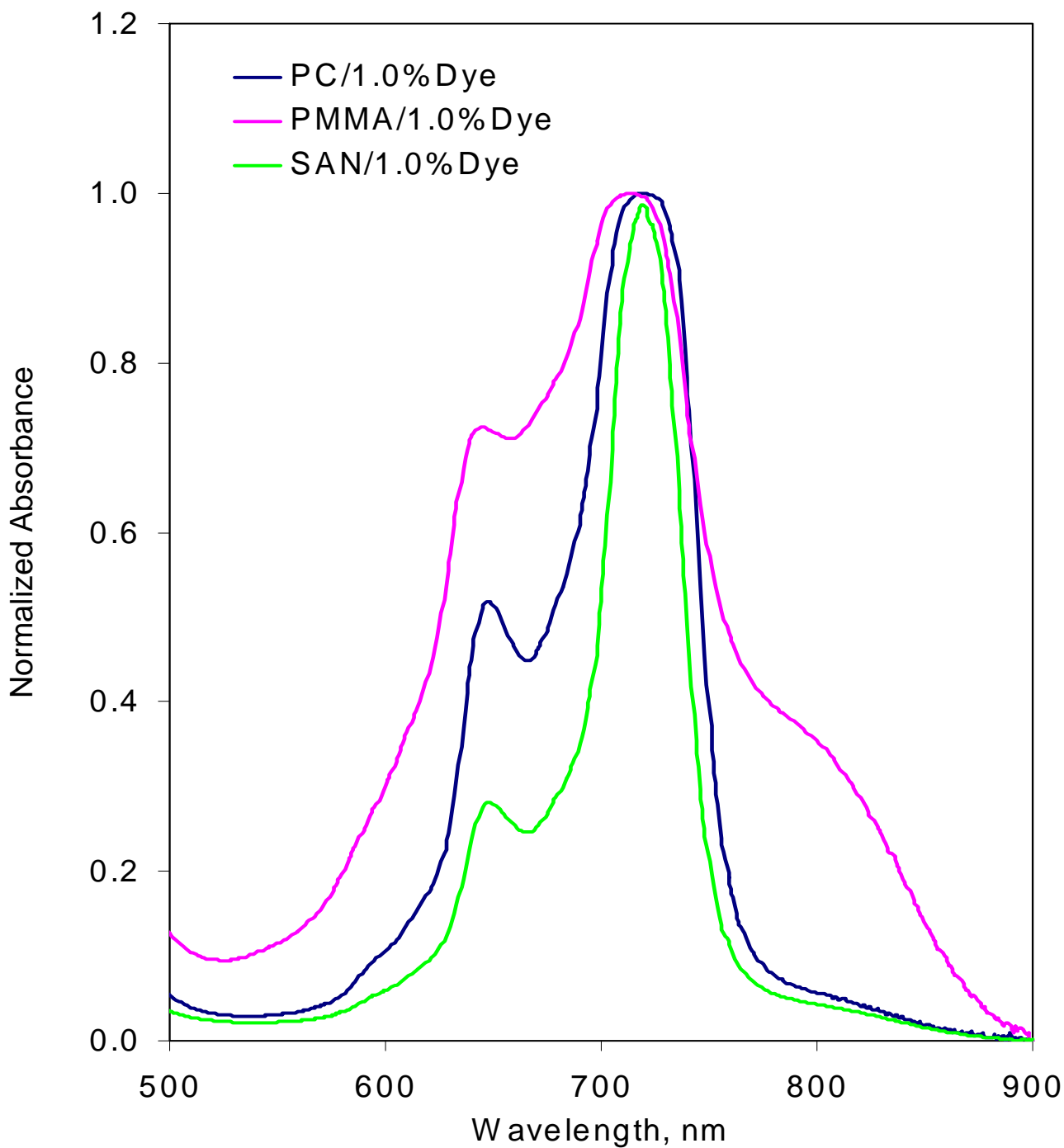


Figure 2

UV/Vis Spectra of Various Polymer/PbPc(CP)₄ Dye System

The strong absorption at 719 nm is monomer, the broad shoulder above 800 nm is the dimer

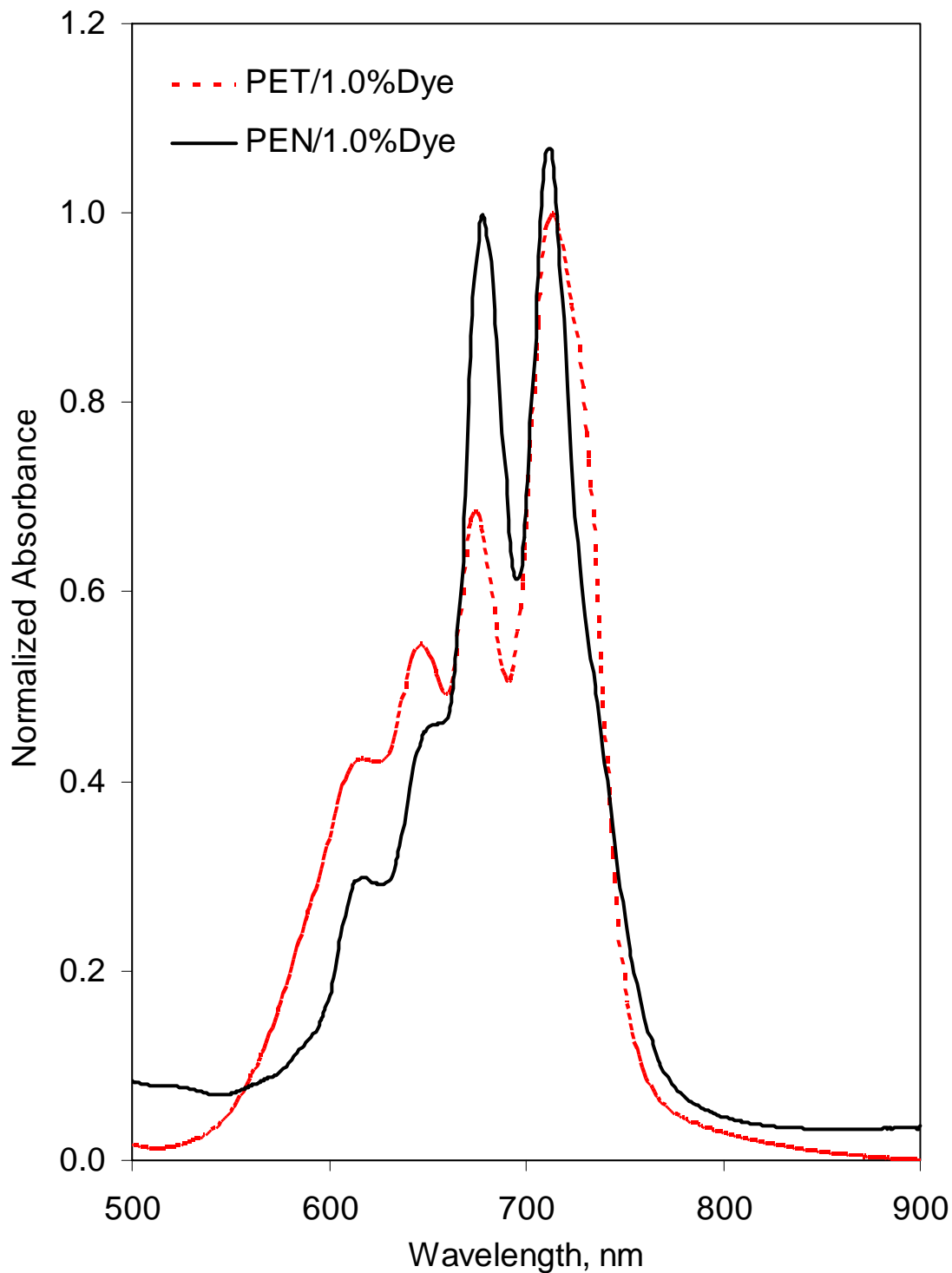


Figure 3

UV/Vis Spectra of Polyester/PbPC(CP)₄Lead Dye Systems-

The appearance of four peaks instead of one peak between 600 and 750 nm indicates formation of metal free dye

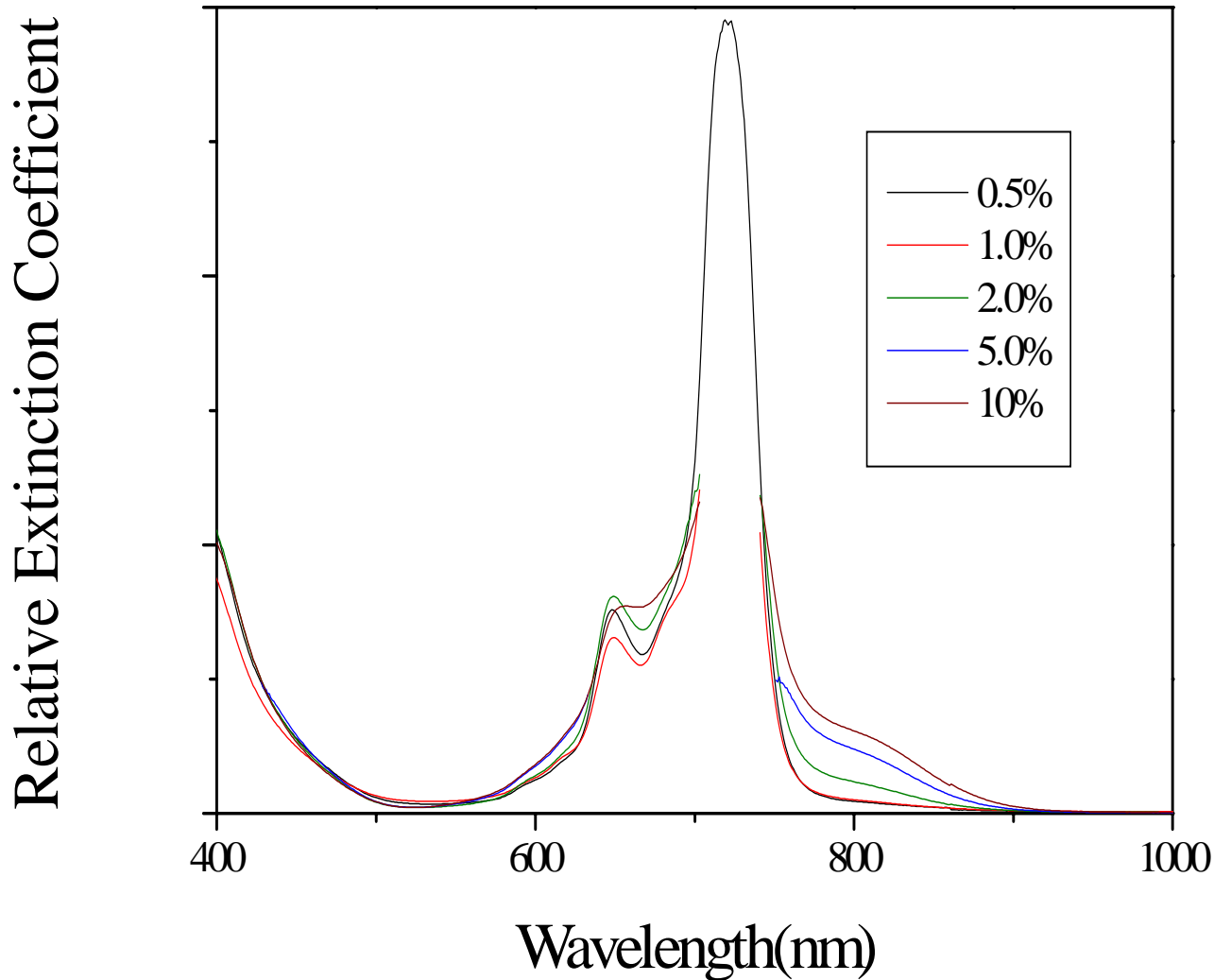


Figure 4

Absorption Spectra of $\text{PbPc}(\beta\text{CP})_4$ in polycarbonate prepared by the new techniques at various concentrations. The strong absorption at 719 nm is monomer, the broad shoulder above 800 nm is the dimer. Optical limiting occurs in the transmission window between about 450 nm and 630 nm

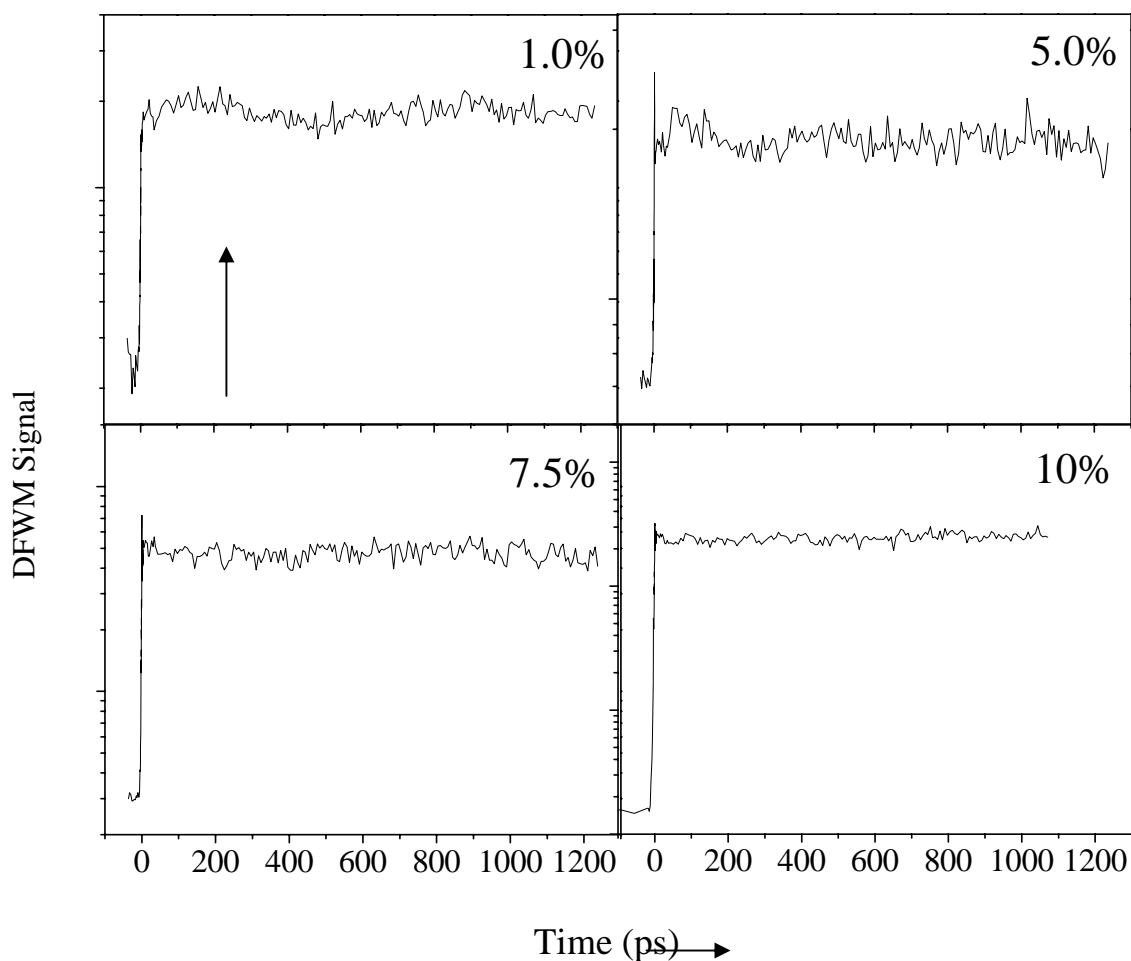


Figure 5

Excited state dynamics of extruded $\text{PbPc}(\beta\text{-CP})_4$ Polycarbonate Films by degenerate four-wave mixing (DFWM) studies. The excited state is formed in less than 10 ps and has a lifetime longer than 20 ns in all the samples even up to 10%. No fluence dependence was detected

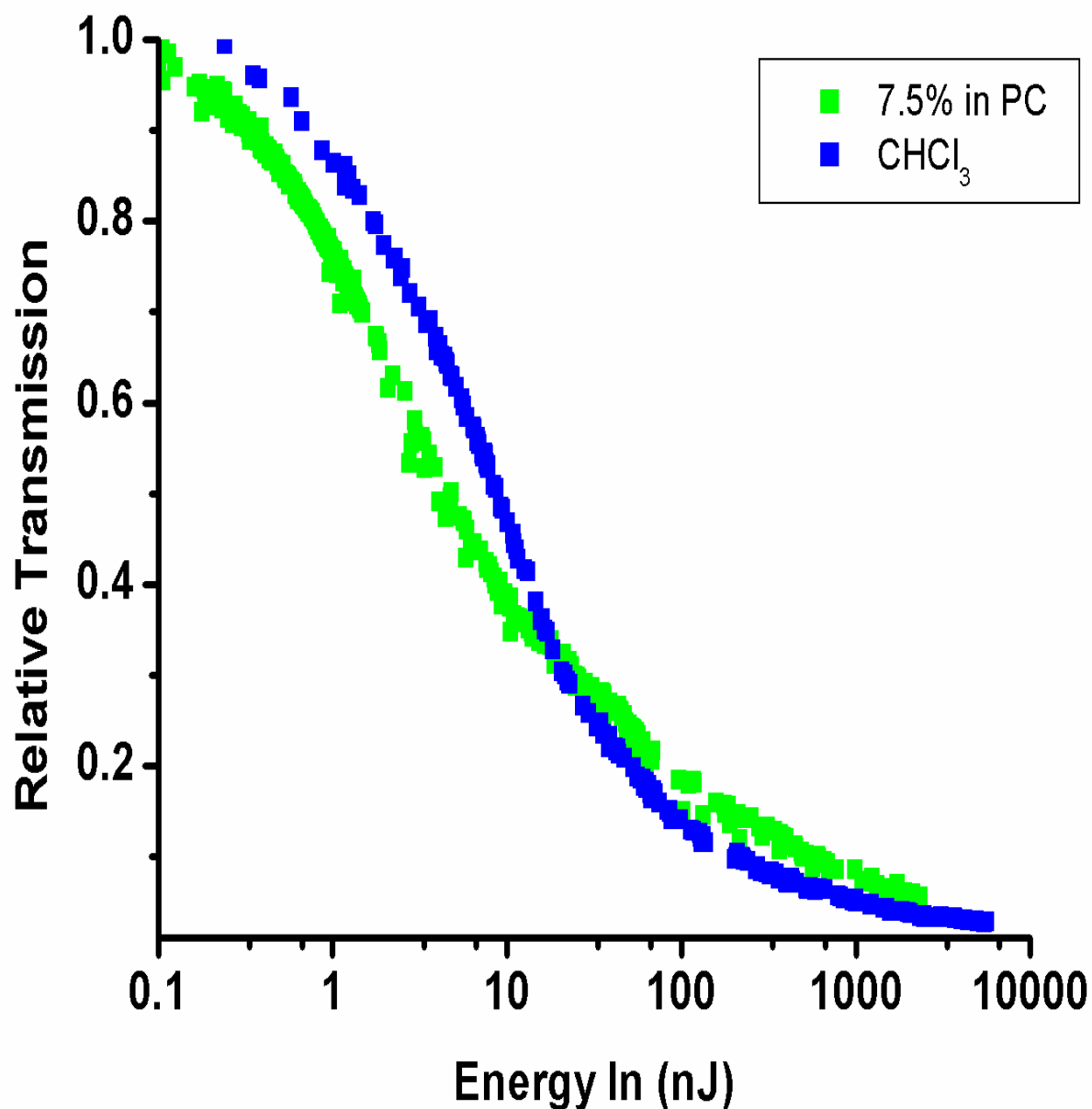
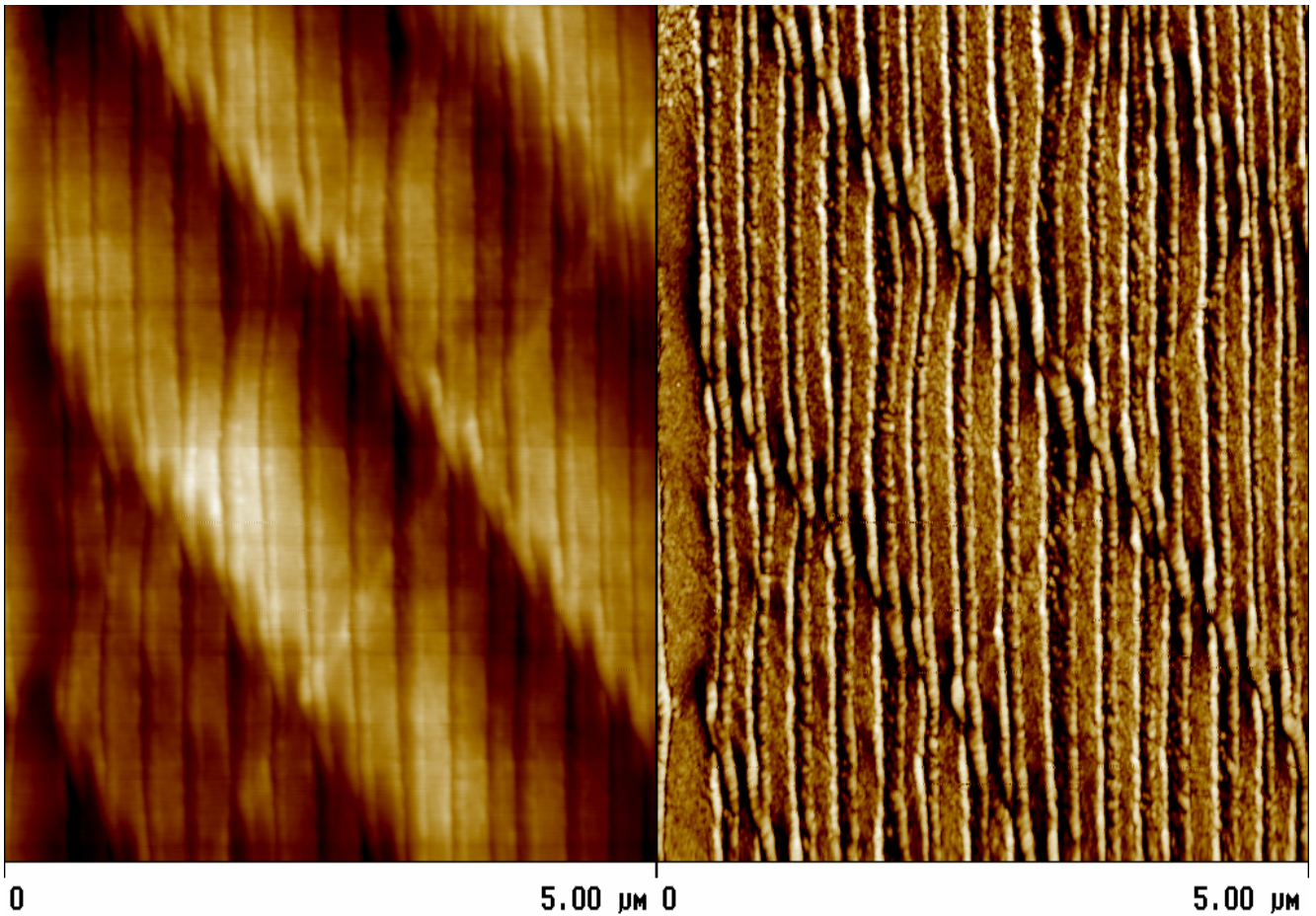


Figure 6

The relative transmission of 7.5% PbPc(β -CP)₄ in polycarbonate vs. the input energy compared to that of a 40 mM solution of this material in CHCl₃. The nonlinear absorption coefficient of the polymer film is larger than that of the solution and the optical limiting threshold is better.



- Expected Average Layer Thickness = 3 mils/512 Layers = 150 microns
- Average Layer Thickness From AFM = 160 microns
- Expected Reflection Wavelength = 1000 nm

Figure 7
Atomic Force Micrographs-150 nm thick PC+7.5% Dye/PET (50/50)

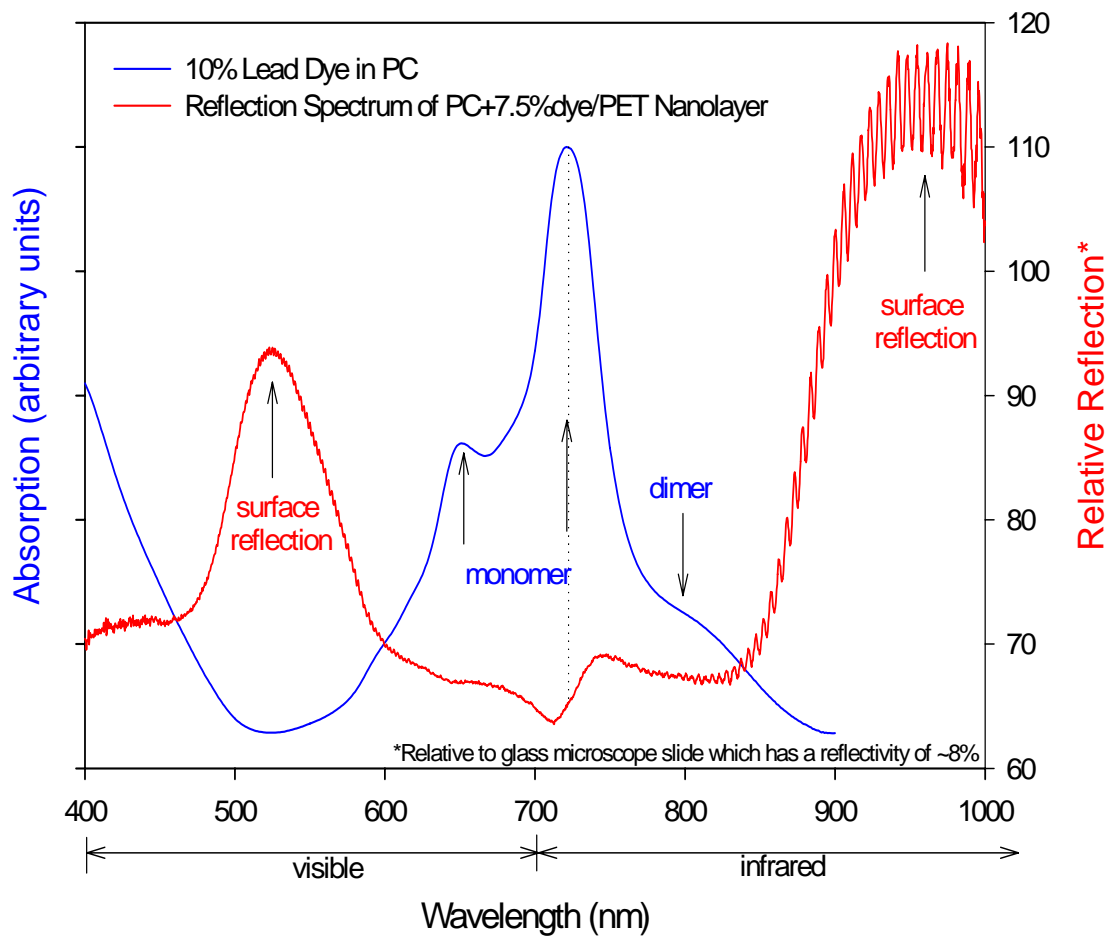


Figure 8
 Selection of good areas for NLO measurements
 PC+7.5% Lead Dye/PET 150 nm thick nanolayers

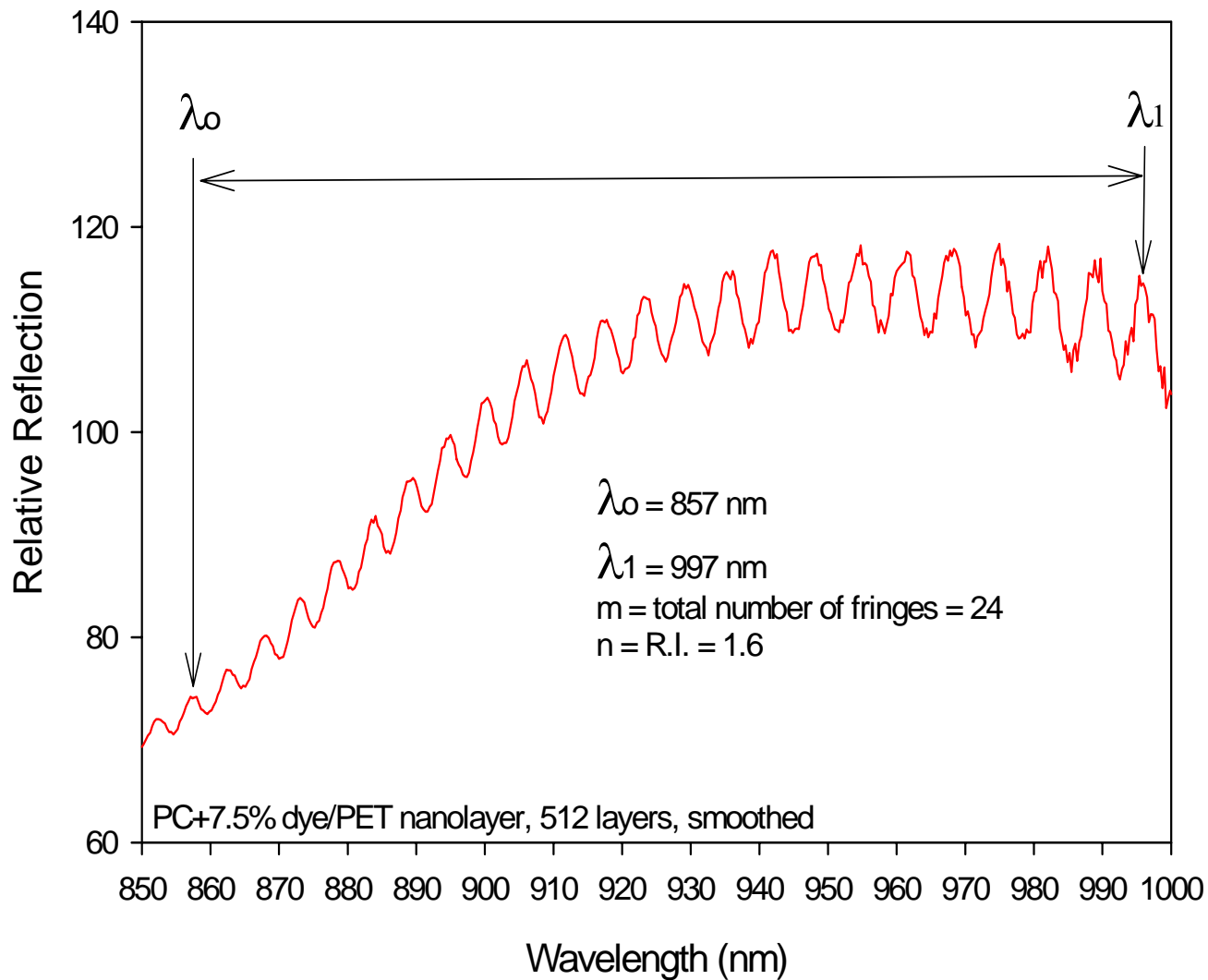
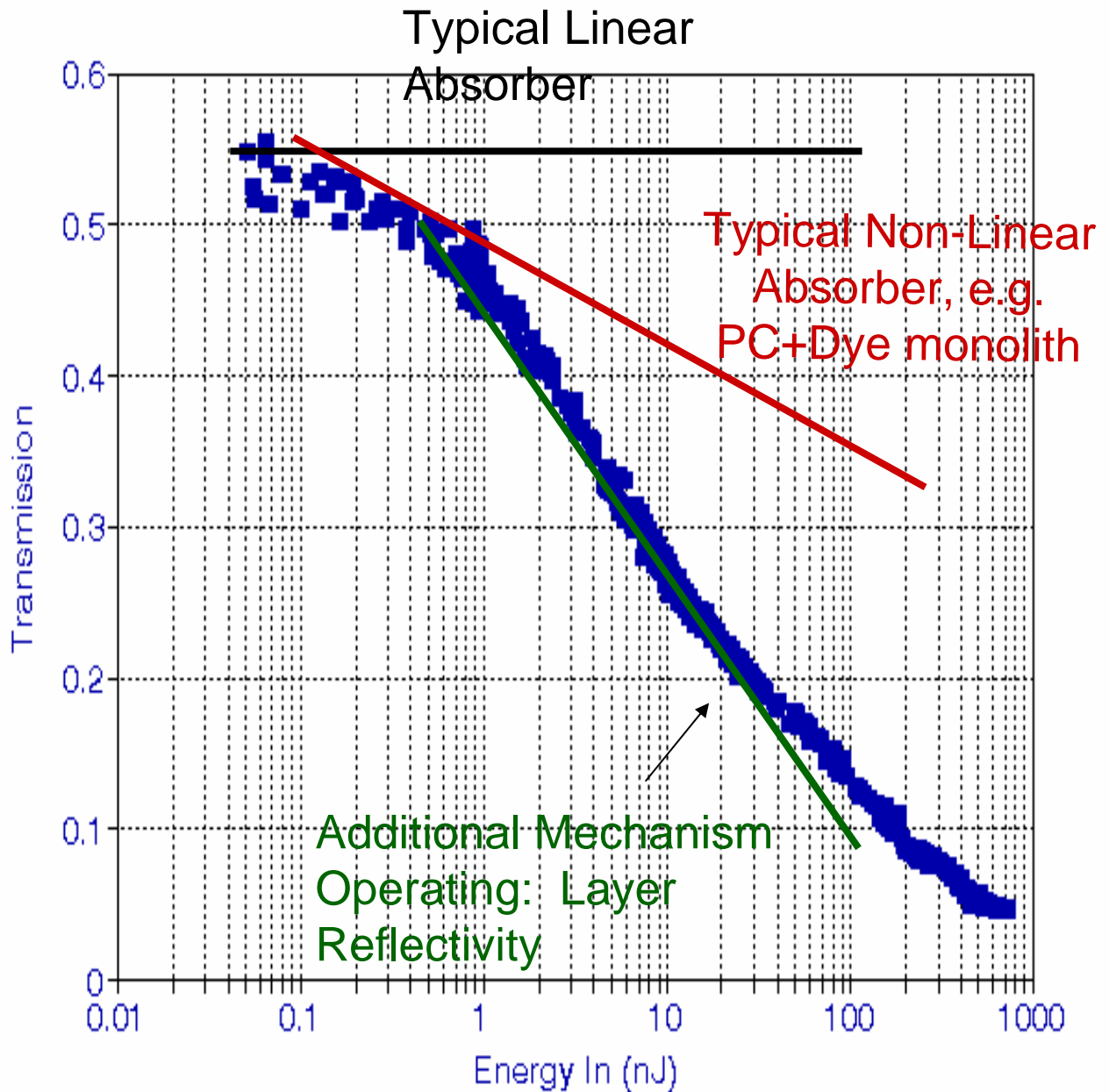


Figure 9
Calculation of total film thickness from the fringes-
PC+7.5% Lead Dye/PET 150 nm thick layers



Wavelength of Laser Used in Test = 532 nm

Figure 10

Nonlinear transmission of an interim nanolayer optical limiter film comprised of 512 layers 120 nm thick alternating 7.5% PbPc(CP)4 in polycarbonate and poly ethylene terephthalate. The photonic band gap in this film is near 750 nm. The transmission of a monolithic film is shown for comparison

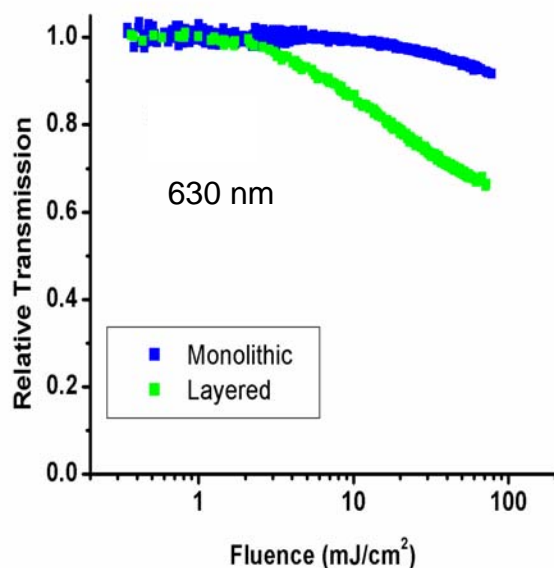
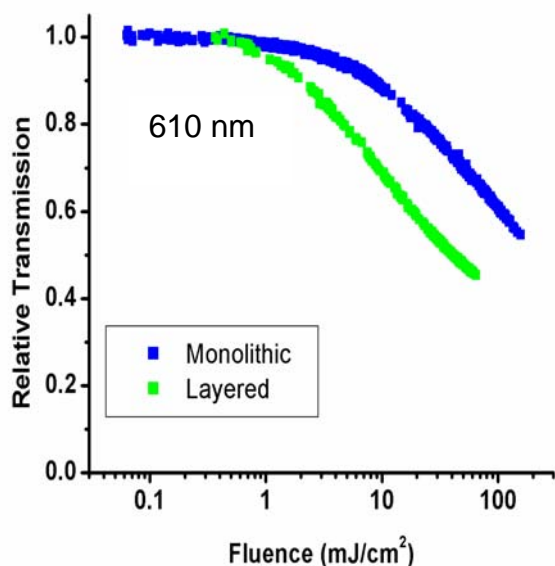
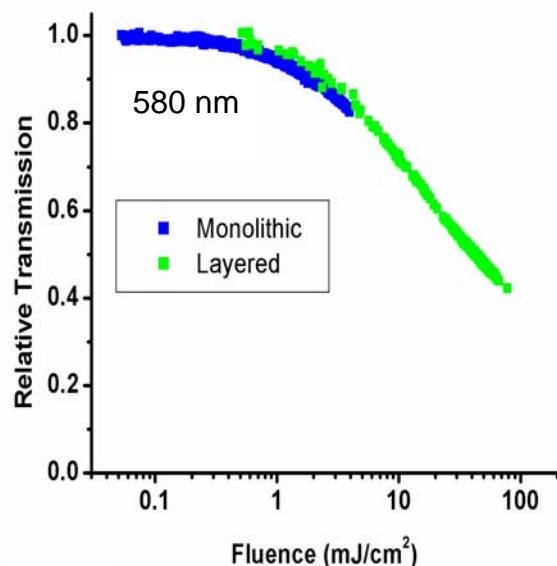
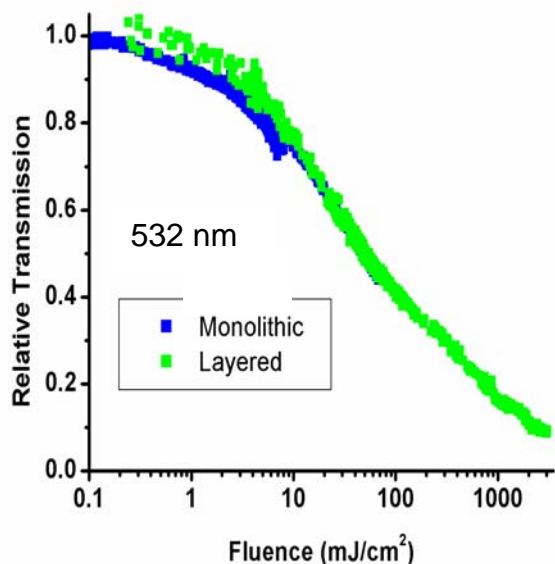


Figure 11

Nonlinear transmission of an interim nanolayer optical limiter film comprised of 512 layers 120 nm thick alternating 7.5% $\text{PbPc}(\text{CP})_4$ in polycarbonate and poly ethylene terephthalate. The photonic band gap in this film is near 750 nm. The transmission of a monolithic film is shown for an approximate comparison

Recent Results

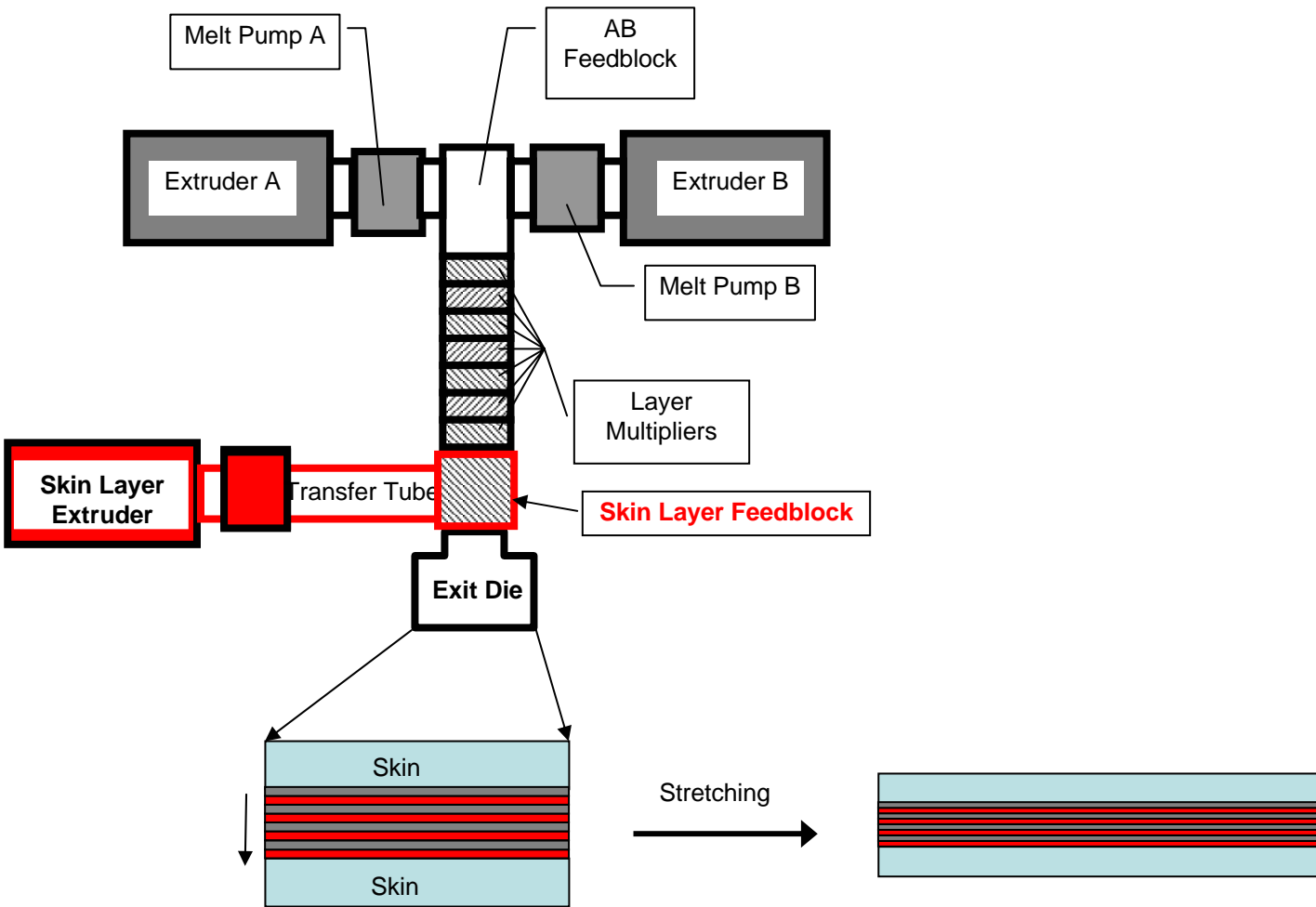


Figure 12

Schematic of the process development which permits insertion of skin layers after the layer-multiplication and just ahead of the exit die

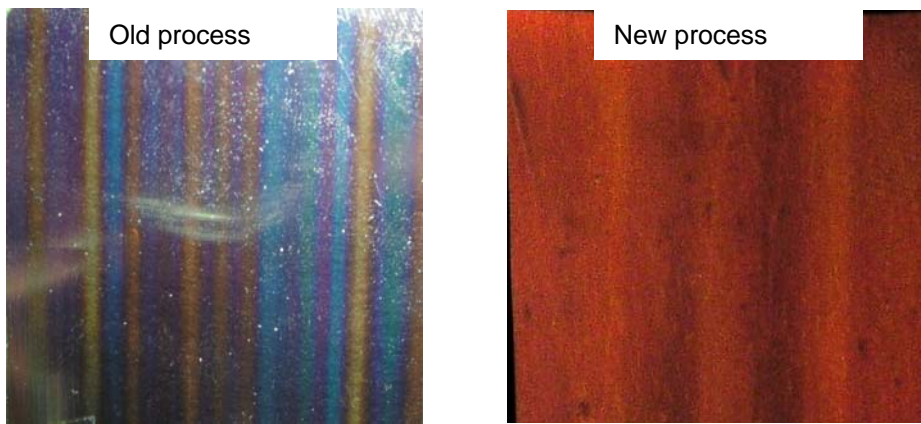


Figure 13
Comparison of 2.5x2.5 cm² areas of PMMA/PS nanolayer films

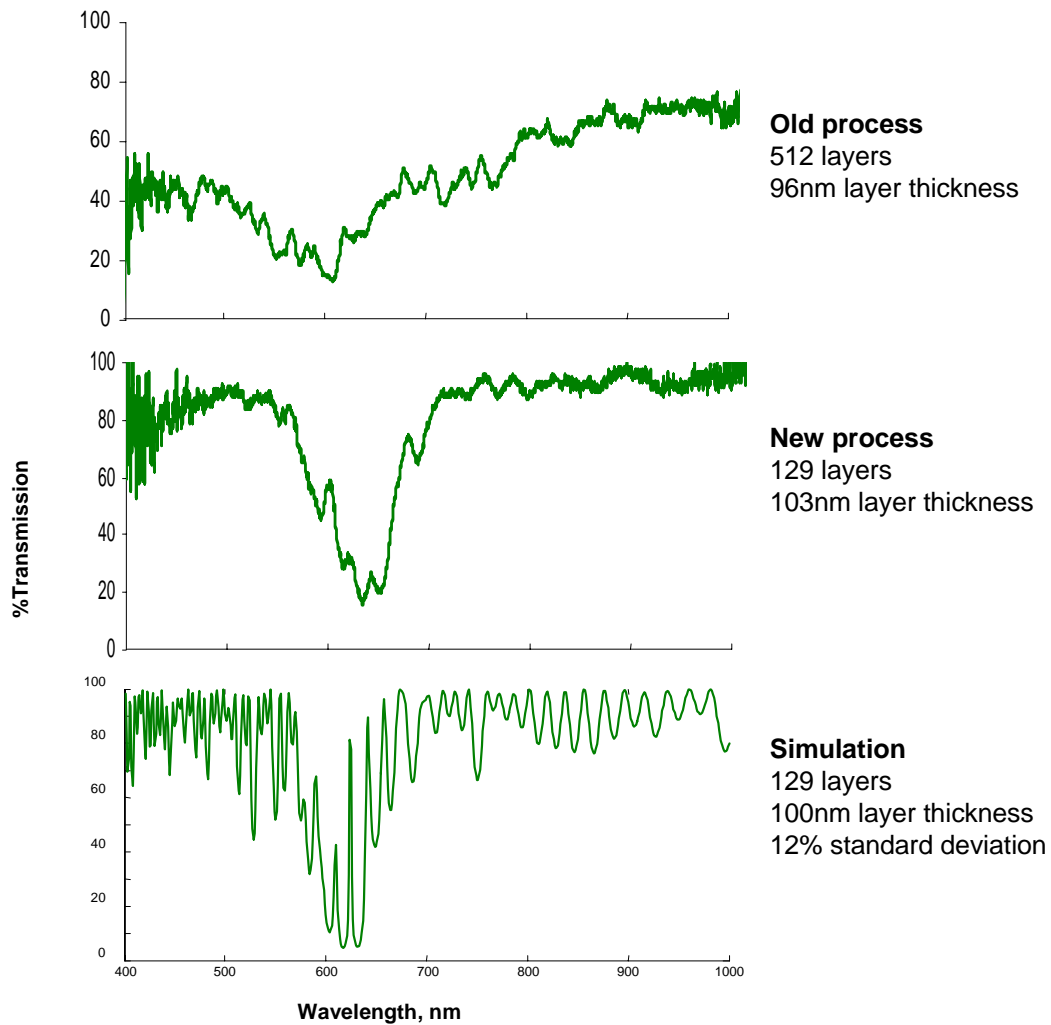


Figure 14
UV/VIS transmission spectra of PMMA/PS nanolayer films

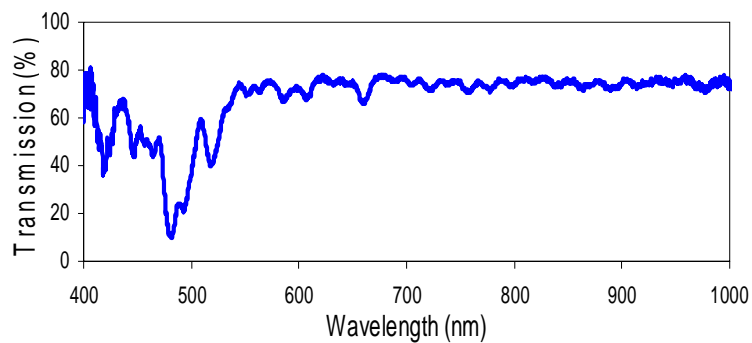
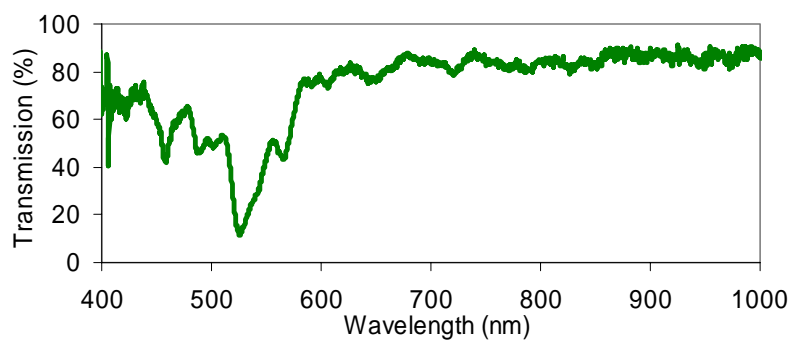
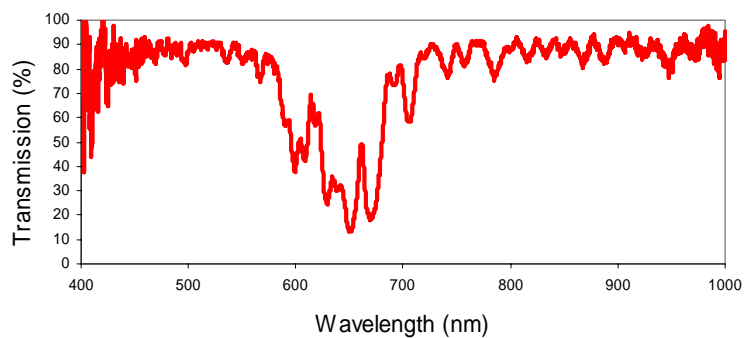
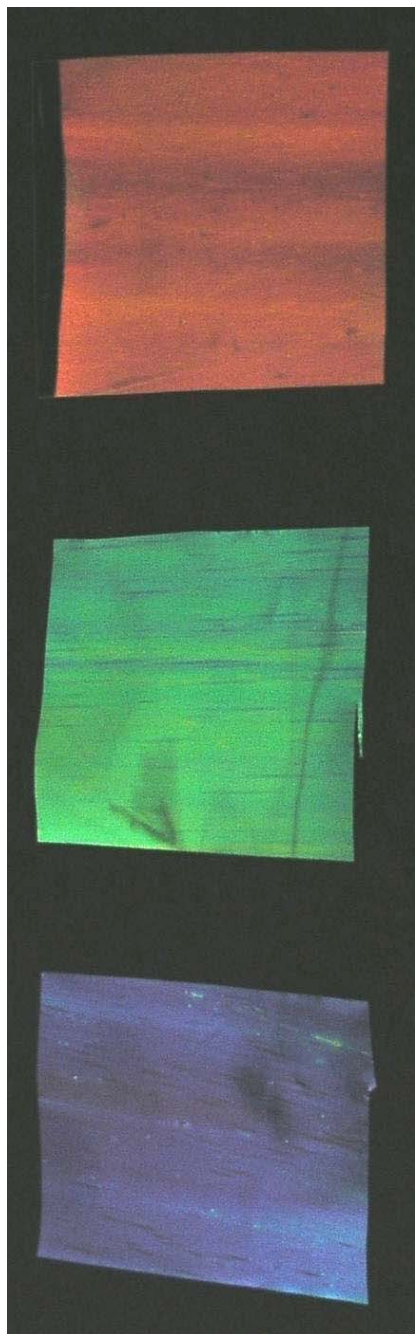


Figure 15

Control of UV/VIS transmission spectra using PMMA/PS nanolayer films

Appendix

The Refractive Index of lead Phthalocyanine/Polycarbonate Composites as a Function of Composition

The Refractive Index of Lead Phthalocyanine/Polycarbonate Composites as a Function of Composition

The concentration dependence of the linear refractive index of a composite polymer made of the polycarbonate, Dow Calibre 200-14, and the nonlinear dye PbPc(CP)₄ was measured. This data is required to design a nonlinear multilayer polymer optical limiter material using this material.

Models for the refractive index of such dye/polymer composites were also investigated. It would be useful to be able to predict the index of other dye/polymer composites.

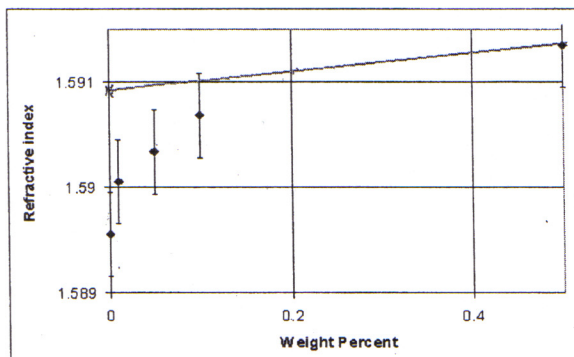
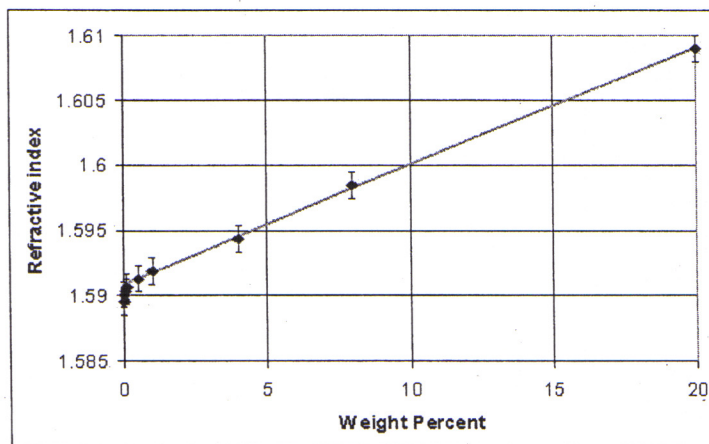
Results: Composite Refractive Index

The refractive index of polymer/dye composites with up to ~20 weight percent dye were measured at six wavelengths between 473 nm and 1546 nm. The samples from pure polycarbonate up to 4% dye were all made using the same fabrication techniques.

The concentration dependence at 532 nm is shown in Figure 1. It is representative of the observed concentration dependence at wavelengths away from the strong absorption bands.

At the concentrations between 0.5% and 20%, the index increases approximately linearly with concentration. This is the concentration regime that is of interest to our optical devices.

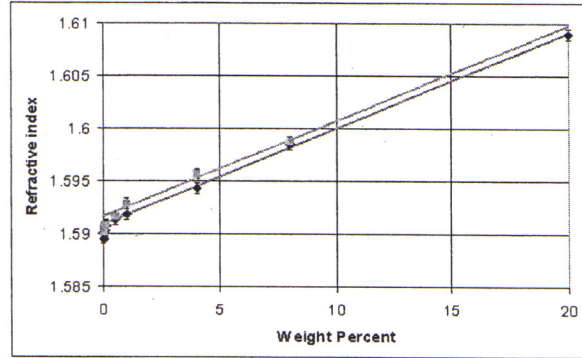
The index deviates from the linear dependence at low dye concentrations. The line from a linear least squares fit does not extrapolate to the index for pure polycarbonate. This is clear in the expanded scale in Figure 2. The measured index for the pure polycarbonate sample is 1.5896 ± 0.0005 . The extrapolated index for the pure polymer is 1.5909 ± 0.0005 . There is a small but significant increase in the index with very small concentrations of phthalocyanine. A similar increase in index was observed at all measured wavelengths except perhaps 1546 nm.



Ageing

It is important for designing optical devices to insure that the refractive index of the composite is stable over time. The stability question is pertinent because some properties, such as the density, of typical polycarbonates have been reported to vary with the time after fabrication.^{1,2} For pure polycarbonate, the reported density changes are on the order of 0.005 over a period of 10^7 to 10^8 seconds. This corresponds to many months to a few years.

Figure 2 shows the effect of ageing on the refractive index of the samples in Figure 1. The index measured a few weeks after fabrication is compared to that about 9 months later. For each dye concentration, the measured index at both times was within the experimental uncertainty of the measurements. However, each of the measured indexes was slightly larger after 9 months. Taking all the data together, a small increase in the index is implied. The least squares fit of the measurements above 0.5% to a straight line gave an intercept of 1.5916 at 9 months, or 0.0007 larger than the intercept for the freshly prepared samples. The slope of the index vs. concentration was almost identical at the two different measurements. Each composite had approximately the same increase in index with time.



Discussion: Model

The approximately linear relationship between the refractive index and the dye concentration suggests that a simple model might be useful for predictive purposes.

At the concentrations of interest for optical applications, the refractive index of an effective medium composite can be related to the properties of the components by well established effective medium models.³ For a phthalocyanine in polycarbonate, the Bruggeman model seems appropriate. In this model the following equation holds.

$$0 = (1 - c) \frac{\rho_A}{\rho} \frac{n_A^2 - n_{eff}^2}{n_A^2 + 2n_{eff}^2} + c \frac{\rho_B}{\rho} \frac{n_B^2 - n_{eff}^2}{n_B^2 + 2n_{eff}^2} \quad (1)$$

This is an implicit equation for n_{eff} , the effective index of the composite, in terms of n_A , and n_B , the refractive index of component A and B respectively and ρ_A , ρ_B , and ρ , the densities of A, B and the composite respectively. Here c is the volume fraction of the component B.

In evaluating this model, the density and the volume fraction of components are required.

Results: Density

In order to apply an effective medium model the density of each of the composite samples was measured. The measurements of the density of the different composites are shown in Figure 4.

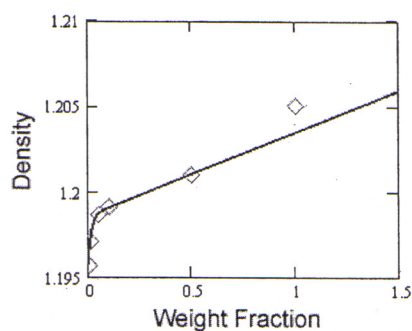
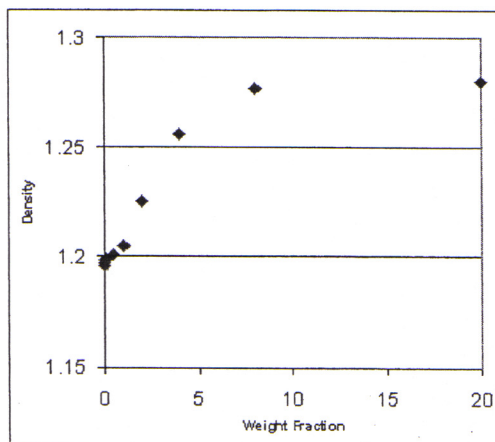
The density of the composite does not vary linearly with dye concentration. The PbPc(CP)₄ dye is known to aggregate at concentrations between 2 and 20%. The dependence of density on concentration in this range may reflect changes in the degree of aggregation of the dye moiety over this range.

Even at concentrations where the PbPc(CP)₄ is monomeric, deviations from linearity are apparent. This is illustrated in Figure 4b which shows the density of the composite on an expanded scale. The line in this figure is a fit of the data to a function of the form:

$$\rho = P_0 + P_1w + P_2e^{P_3w}$$

Where ρ is the density, w is the weight fractions and the P_n are fitting constants.

We noted a similar dependence of the refractive index on concentration in Figure 2. In the next section, the relationship between the density and the refractive index of a material is discussed.



Density Dependence of the Refractive Index

The observed variations in the index and density of these composites suggested they are correlated. Here a quantitative correlation is discussed.

The variation in refractive index with density of a polymer can be found by considering the molar polarization P_m :

$$P_m = \frac{M}{\rho} \left(\frac{\epsilon - 1}{\epsilon + 2} \right) \quad (2)$$

where M is the molecular weight, ρ the density and ϵ the dielectric constant. If we assume P_m is constant with a density change, we can solve for the dielectric constant as a function of density:

$$\epsilon = \frac{1 + 2C\rho}{1 - C\rho} \quad (3)$$

where $C = P_m/M$ is a constant for a particular material. Since the index of refraction, n , is $\epsilon^{1/2}$, the index as a function of density is:

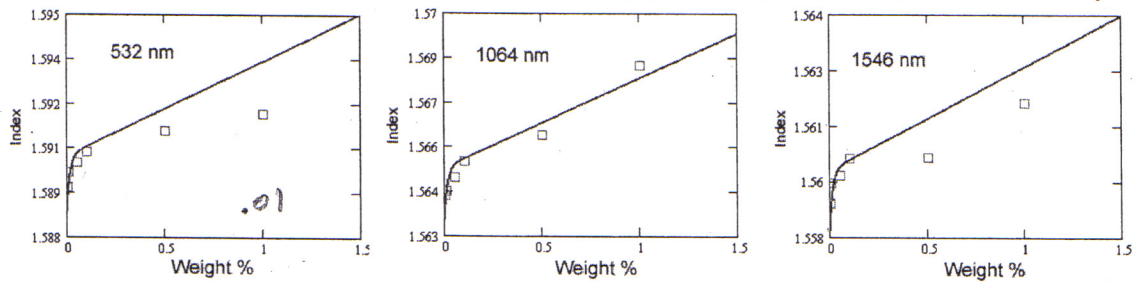
$$n(\rho) = \left(\frac{1 + 2C\rho}{1 - C\rho} \right)^{1/2} \quad (4)$$

and the coefficient C can be found from:

$$C = \frac{(n_0^2 - 1)}{(n_0^2 + 2)\rho_0} \quad (5)$$

For a typical polymer with $n_0=1.5$ and $\rho_0=1.0$. The value of $C = 0.294$ and $dn/d\rho = 0.59$.

The observed refractive indexes at each wavelength were fit to equation 4 using n_0 and ρ_0 (equation 5) as fitting parameters and the density as function of concentration from Figure 4. Figure 5 shows the calculated and observed index for the lowest concentration composites. The calculated indexes (blue line) are within the uncertainty of



the experimentally measured indexes.

The index of the composite appears follow the measured density up to about 0.5% to 1% by weight. We can conclude that the nonlinear dependence of the index on concentration shown in Figure 2 can be traced back to the density of the composite.

Composite Density/Specific Volume

At low phthalocyanine concentrations the density increase in the polycarbonate can account for the refractive index of these composites. At higher concentrations, the phthalocyanine will contribute to the refractive index of the composite. In this regime, the index of the composite should be modeled by effective medium theories.

In order to apply effective medium theories, such as Eqn. 1, the densities of the individual components are required. In the polymer literature, the specific volume, $V = 1/\rho$, where ρ is the density is the relevant quantity. For an ideal composite, the specific volumes are additive:

$$V_M^{ideal} = wV_P + (1-w)V_A \quad (6)$$

where V_M , V_P , and V_A are the specific volumes of the mixture, polymer and additive respectively and w is the weight fraction of the additive.

The specific volumes corresponding to the measured densities above are shown in Figure 6 and compared to an ideal solution.

Experimentally, the measured densities of the composites indicate that the phthalocyanine/polycarbonate composites are not ideal solutions; they do not follow Eqn. 6.

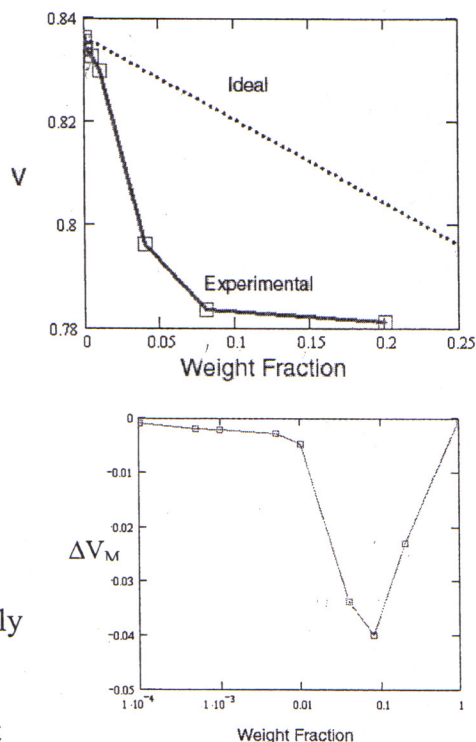
The deviation from ideal is measured by the excess specific volume, ΔV_M , is the difference between the observed, V_M^{obs} , and ideal specific volumes.

$$\Delta V_M = V_M^{obs} - V_M^{ideal} \quad (7)$$

Figure 7 shows a plot of the excess specific volume of the polycarbonate/phthalocyanine composite. There is a substantial negative deviation in the specific volume from the ideal even at very low concentrations of dye an almost 5% deviation at around 10 weight percent.

The large deviation in the specific volumes from ideality in these composites is probably due to specific interactions between the phthalocyanines and polycarbonate. Apparently, the $PbPc(CP)_4$ dye interacts with the polycarbonate host to cause a decrease in the free volume.

The increase in density is qualitatively consistent with the phthalocyanine behaving as an anti-plasticizer for the polycarbonate. The effect is well known.⁴ Antiplasticizers typically cause a decrease in free volume and a densification of the polymer. Models for the change in specific volume with the addition of an antiplasticizer to polycarbonate have been proposed. However, an evaluation one of these models⁵ show that the increase in density for the $PbPc(CP)_4$ is much larger than is expected.



We conclude that there is probably a specific interaction between the PbPc(CP)₄ dye and the polycarbonate. If there are specific interactions, the concentration dependence of the density of the composites will be characteristic for each dye/polymer combination.

Model: Refractive index of the composite

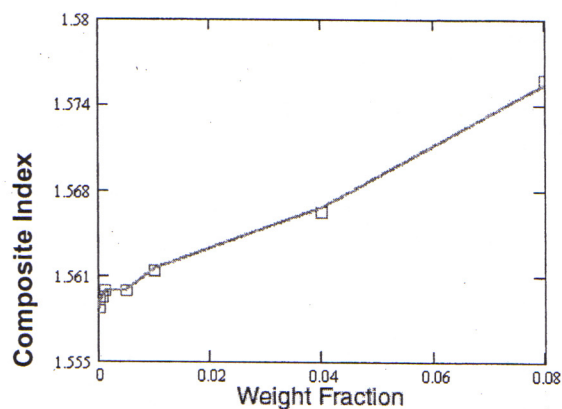
In order to evaluate the Bruggeman model, Eqn. 1, in a case where the composites are far from ideal solutions, we can assume that all the non-ideality is in the polymer component.

The density of the polymer, ρ_A , and the partial specific volume, V_P^* , in a composite are taken to be:

$$\frac{1}{\rho_A} = V_P^* = V_P + \Delta V_M \quad (9)$$

Since the excess volume, ΔV_M , of the composite is negative, ρ_A , was larger than the density of pure polymer. The refractive index of the polymer component, n_A , was calculated from ρ_A using the equation derived above. The density of the phthalocyanine, ρ_B , was taken to be the density of pure phthalocyanine and n_B was varied to find the best fit to the data.

This computed index of the composite using $n_B = n_{Pc} = 1.575$ is compared to the experimental data at 1546 nm in Figure 8. The agreement is good.



Summary

The concentration dependence of the refractive index of a polycarbonate/PbPc(CP)₄ composite is approximately linear over the concentration regime (1% to 20% by weight) of interest for multilayer polymer for optical devices. The specific equation is:

$$n = 1.5909 + 9.06 \times 10^{-4} * w \quad (10)$$

where w is the weight fraction of the PbPc(CP)₄.

The intercept in equation 10 differs from the measured index for pure polycarbonate, 1.5896 ± 0.0005 . The difference is ascribed to a difference in density between pure and dyed polycarbonate even at dye concentrations of less than 0.1% by weight dye.

The index of the composites showed a small change over time. They increased by only about 0.0007 after about nine months. The slope of the index vs. the concentration did not change measurably with time. The reflectivity of a multilayer dielectric stack depends on the refractive index contrast between the layers. The differential changes in the index of the layers would be within the experimental uncertainty of this measurement over the nine month interval.

The observed index of the composites could be modeled using a Bruggeman model for effective media so long as the deviation of the density (specific volume) from ideality was taken into account.

The dependence of the density of the composite on dye concentration was not simple. Measurable negative excess specific volume were found for composites with less than 0.1% by weight dye and a negative excess specific volume of almost 5% of the specific volume was observed at concentrations near 10% by weight. The phthalocyanine molecule causes a concentration dependent densification of the polycarbonate in the composite materials. Qualitatively, the phthalocyanine acts as an antiplasticizer for the polycarbonate. However, the observed changes in the specific volume (density) were much larger than predicted by models for the change in specific volume with the addition of an antiplasticizer to polycarbonate.

The densification probably results from specific interactions between the phthalocyanine and the polycarbonate. At the lowest concentrations, processing may also have an influence.

The functional dependence of the refractive index on concentration depends upon the partial specific volume (density) of the components. Since the density appears to depend on the magnitude of specific interactions between the PbPc(CP)₄ dye and the polycarbonate host, it is not clear if the dependence found here will apply to other phthalocyanines, other classes of nonlinear dyes, or other polymer hosts.

1 C.G. Robertson and G.L. Wilkes; *Macromolecules* **33**, 3954 (2000)

2 R. Wimberger-Friedel and J.G. de Bruin; *Macromolecules* **29**, 4992 (1996)

3 R.J. Gehr, G.L. Fischer, and R.W. Boyd; *J. Opt. Soc. Am. B*; **14**, 2310 (1997)

4 J.S. Vrentas, J.L. Duda and H.-C. Ling; *Macromolecules*; **21**, 1470 (1988)

5 F.A. Ruiz-Trevino and D.R. Paul; *J. Polymer Sci., Part B, Polym. Phys.*; **36**, 1037 (1998)